

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 November 2000 (30.11.2000)

PCT

(10) International Publication Number
WO 00/71635 A1

(51) International Patent Classification⁷: C09K 7/02,
C08K 5/098, C08L 33/24

(21) International Application Number: PCT/US00/13727

(22) International Filing Date: 19 May 2000 (19.05.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/316.527 21 May 1999 (21.05.1999) US
60/165.789 16 November 1999 (16.11.1999) US

(71) Applicant: CABOT CORPORATION [US/US]; 75 State
Street, Boston, MA 02109-1806 (US).

(72) Inventors: MILLER, Edward, E.; 6417 Rainier Road,
Plano, TX 75023 (US). BENTON, William, J.; 16723
Cimarron Drive, Magnolia, TX 77355 (US).

(74) Agent: LANDO, Michelle, B.; Cabot Corporation, 157
Concord Road, P.O. Box 7001, Billerica, MA 01821-7001
(US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CZ, DE, DK,
DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,
LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ,
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT,
TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMER COMPOSITIONS

(57) Abstract: Novel polymer compositions are disclosed, along with their use as well service fluids, for example as completion fluids, work-over fluids or drilling fluids, comprising water soluble copolymers having sulfonate groups and carboxylate groups, along with alkali metal salts of carboxylic acid. Exemplary copolymer has 5 to 95 wt.% structural units derived from 2-acrylamido-2-methylpropanesulfonic acid or salt thereof, and 5 to 95 wt.% structural units derived from acrylic acid or salt thereof. A salt of polymer may be used, such as the sodium, potassium, ammonium and calcium salts. Exemplary alkali metal salts of the polymer composition include sodium, potassium and cesium salts of formic acid and/or acetic acid in amounts suitable to develop high temperature viscosity suitable for such well servicing fluids. The polymer composition is hydratable/soluble in a brine of sodium and/or potassium and/or cesium salts of formic and/or acetic acid.

WO 00/71635 A1

POLYMER COMPOSITIONS

5

INTRODUCTION

This invention relates to certain polymer compositions, their preparation and their use as viscosifiers in alkali metal salt solutions which are particularly useful in viscosifying well-drilling fluids for oil field operations at temperatures above 350°F.

DESCRIPTION

It is known to use aqueous polysaccharide compositions in well-drilling operations, e.g. in oil and gas wells. Examples of polysaccharides include cellulose derivatives, such as carboxyethylcellulose, carboxymethylcellulose, carboxymethylhydroxyethylcellulose, alkylhydroxyalkylcelluloses, alkylcelluloses, alkylcarboxyalkylcelluloses and hydroxyalkylcelluloses (particularly hydroxyethylcellulose); and microbial polysaccharides such as Succinoglycan polysaccharides, Scleroglucan polysaccharides and Xanthan polysaccharides.

In order to achieve suitable density for use in well-drilling operations, it is conventional for the known aqueous polysaccharide compositions to include water soluble salts, e.g. as described in UK Patent No. 1,549,734. These salts are typically halide salts (e.g. chlorides and bromides) of mono- or divalent cations, such as sodium, potassium, calcium and zinc, e.g. sodium chloride, potassium chloride, calcium bromide or zinc bromide.

One problem faced in drilling operations relates to thermal stability of well service fluids such as completion fluids, work-over fluids and drilling fluids. Temperatures in subsurface formations generally rise approximately 1 degree C. per hundred feet (30 meters) depth. Any aqueous polysaccharide

composition has its own characteristic temperature above which it undergoes severe chemical degradation with undesirable reduction of viscosity, thus imposing limitations upon its use in drilling operations below a corresponding depth.

5 Additives, for example blends of polymeric alkaline materials such as that sold by International Drilling Fluids (UK) Ltd., under the trade mark "PTS 200," have been used to improve thermal stability of aqueous polysaccharide compositions.

Polymer compositions have now been found that have excellent
10 thermal stability and excellent performance characteristics for use in well service fluid applications. Novel polymer / alkali metal carboxylate compositions disclosed here are suitable for use in aqueous well servicing fluids and incorporate high molecular weight copolymer soluble in brine. Adding salt to a solution of polymer in water is a known method of removing
15 the polymer from solution. The highest molecular weights will come out of solution first and, as more and more salt is added, lower and lower molecular weight polymers come out of solution. In contrast, in the novel aqueous polymer compositions disclosed here, the high molecular weight copolymer, further described below, is sufficiently soluble in brine comprising alkali metal
20 carboxylate to develop suitable high temperature viscosity, that is, viscosity at the elevated temperatures encountered by well drilling fluids. Moreover, in accordance with at least certain preferred embodiments, the polymer compositions have "durable" viscosity, that is, advantageous density and excellent high temperature viscosity is maintained even after prolonged
25 working of the well service fluid. The polymer compositions disclosed here comprise water soluble copolymer having functionality which includes at least sulfonate groups and carboxylate groups. The copolymer is sufficiently soluble in saturated and other high concentration brines of alkali and metal

salt(s) of carboxylic acid(s), for example, cesium formate brine, to provide polymer compositions having good density and excellent high temperature viscosity for well servicing fluids.

According to one aspect of the present invention, there is provided
5 aqueous polymer compositions comprising the aforesaid copolymer having at least sulfonate group and carboxylate group functionality, dissolved in brine for use as well service fluids, such as completion fluids, work-over fluids and drilling fluids. Preferably, such soluble copolymer is the polymerization reaction product of acrylamidomethylpropanesulfonic acid or salt thereof with
10 acrylic acid and/or alkali metal salts or ammonium salts of carboxylic acid or other suitable unsaturated carbonyl compounds.

In accordance with another aspect, an aqueous polymer composition comprises water soluble copolymer having functionality including at least sulfonate groups and carboxylate groups, and alkali metal salt of carboxylic
15 acid.

It will be apparent to those skilled in the art that incidental quantities of other salts, such as sulfates, nitrates and bicarbonates, may also be present in compositions of the invention, and inevitably will be present in compositions where sea water or other naturally occurring brine is used in preparing the
20 composition. If desired the composition may also contain an antioxidant, e.g. 2-mercaptobenzothiazole and/or other suitable additives. When 2-mercaptobenzothiazole is used it may conveniently be incorporated in the same proportion, w/v, as the water soluble copolymer. Those skilled in the art will appreciate that 1% w/v corresponds to a concentration of 10 kgm.sup.-3
25 (10 g/l) of composition. It is advantageous for the pH of the composition to be preferably greater than 8.0, but not higher than 11.5, preferably at least 9.0 and less than 10.5, for reasons of stability and reduced corrosiveness of the composition. The pH may be controlled by addition of suitable reagents, e.g.

sodium hydroxide. The presence of a monovalent salt, e.g., a carbonate salt, e.g. potassium carbonate or cesium carbonate, in the composition can enable a suitable buffering effect to be achieved.

5 The invention also provides a process of preparing an aqueous polymer composition of the invention. In accordance with one aspect, the alkali metal salt of carboxylic acid is added to an aqueous composition, optionally a brine composition, in which the water soluble copolymer is already dissolved and hydrated. In accordance with one preferred embodiment, the alkali metal salt of formic, acetic and/or other suitable carboxylic acid is added to an aqueous
10 composition containing the water soluble copolymer with, when present, other salts and/or other ingredients, etc. In accordance with an alternative embodiment, the polymer composition described above comprising the water soluble copolymer and the alkali metal salt of carboxylate acid, optionally with other dry ingredients, intended for use in a well service fluid, is provided as a
15 dry powder to which water or brine solution is added to hydrate the polymer and dissolve the alkali metal salt of carboxylic acid. In accordance with another alternative embodiment, the water soluble copolymer is added to a brine comprising the alkali metal salt.

20 In accordance with certain preferred embodiments, the brine employed in an aqueous polymer composition of this invention contains primarily sodium or potassium salt of carboxylic acid, although as mentioned above, other salts may be present in trace or minor amounts. Typically, such brines are substantially saturated solutions of the sodium or potassium salt. In other preferred embodiments, the cesium salt of carboxylic acid is used with only
25 trace or minor amounts of other salts. Such cesium brines provide aqueous polymer compositions of higher density than corresponding compositions employing sodium or potassium brines. More specifically, for example, aqueous polymer compositions of the invention employing cesium brines

above about 40% to 43% w/w (i.e., 4 parts by weight of cesium salt to 10 parts by weight of water used in the polymer composition) have density equal to or greater than corresponding compositions employing substantially saturated potassium brine. Thus, in accordance with certain especially preferred
5 embodiments, aqueous polymer compositions of the invention employ the water soluble copolymer in a cesium formate brine or other suitable brine of cesium carboxylate, with at most only trace or minor amounts of other salts (i.e., such as might be contributed by sea water), and the cesium salt is used in an amount from about 40% to fully saturated.

10 In accordance with another aspect, there is provided the use of a polymer composition of the invention as a well service fluid, especially as a completion fluid, a work-over fluid or drilling fluid in a well-drilling operation. Preferably, the water soluble copolymer has a weight average molecular weight of at least about 1,000,000, preferably from 1,000,000 to
15 5,000,000, more preferably 1,500,000 to 3,000,000. In that regard, it is a significant advantage of the present invention, that at least preferred embodiments of the aqueous polymer compositions disclosed here provide well servicing fluids which develop high viscosity, i.e., have an improved and retained viscosity at temperatures up to at least 425°F. Moreover, it is a
20 notable advantage of the present invention that such preferred embodiments retain their excellent viscosity characteristics at elevated temperature even after extended use as a completion or drilling fluid. In certain preferred embodiments, the copolymer is soluble in a saturated alkali metal carboxylate brine solution, e.g., is a substantially saturated cesium formate solution, in an
25 amount of at least about 4 lbs/bbl, more preferably at least 6 lbs/bbl. Certain such preferred embodiments have retained viscosity at temperatures up to at least about 425°F after 700hours of extended use as a well service fluid, as tested and defined by "*Recommended Practice Standard Procedure for Field*

Testing Water-Based Drilling Fluids" API Recommended Practice 13B-1 (RP 13B-1) First Edition, June 1, 1990 (American National Standard, ANSI/API RP 13B-1-90 Approved: July 12, 1993) . Certain such preferred embodiments employing the high molecular weight, water soluble copolymer described
5 above in an amount of 0.05 to 5 wt.% (based on the total weight of all solids components of the polymer composition) and the alkali metal carboxylate in an amount of 95 to 99.95 wt.% (also based on the weight of all solids components) to produce a substantially saturated or other concentration brine, to provide a well-servicing fluid which develops an apparent viscosity greater
10 than or equal to 20 cPs., a plastic viscosity of greater than or equal to 15 cPs, and a yield point of greater or equal to 5 lb./100 ft² when dissolved in alkali metal formate brine at a concentration of 2 pounds per barrel and measured at 120 degrees F. In accordance with certain highly preferred embodiments, the well-servicing fluid retains at least 50% of its apparent viscosity after roller
15 aging for 30 days at 375 degrees F and measured at 120 degrees F. Suitable water soluble copolymers can be prepared in accordance with the teachings of published European patent application No. EP 0068189, the entire disclosure of which is hereby incorporated by reference.

The alkali metal salt of carboxylic acid preferably is selected from the
20 sodium, potassium and cesium salts of suitable carboxylic acids, preferably C1 to C3 carboxylic acid, most preferably the sodium, potassium and/or cesium salts of formic acid, acetic acid or mixtures thereof that are blended to obtain the desired density of the drilling, completion, workover or packer fluid. In accordance with certain preferred embodiments, substantially saturated brine
25 of sodium formate, sodium acetate, potassium formate and/or potassium acetate is used. In accordance with other preferred embodiments, the brine is a 40% w/w or high solution of cesium formate and/or cesium acetate. In accordance with certain highly preferred embodiments, at least about 5 wt.%

of the alkali metal salt of carboxylic acid is the cesium salt. Such
embodiments are found to provide well service fluids having high density and
unexpectedly advantageous density and durable viscosity. In that regard, the
cesium brines at about 43% of saturation are found to provide densities equal
5 to the density of substantially saturated potassium brines. At concentrations
higher than 43%, the cesium brines advantageously provide even high
densities, such as 2.18 to 2.3. As noted above, it is a significant and
unexpected advantage of the polymer compositions disclosed here, that they
are sufficiently water soluble to yield durable, high temperature viscosities
10 suitable for well servicing fluids, in saturated brines of alkali metal
carboxylates or in brines having salt concentrations less than saturation but
sufficiently high to provide necessary density levels. It is significant and quite
unexpected, for example, that the water soluble copolymers disclosed above,
having a weight average molecular weight of 1,000,000 to 5,000,000 are
15 soluble at least to levels of 0.05 to 5.0 wt.% (based on the weight of all solids
contents of the polymer composition) in an 80% brine or higher of alkali metal
carboxylate, yielding an apparent viscosity greater than or equal to 20 cPs., a
plastic viscosity of greater than or equal to 15 cPs, and a yield point of greater
or equal to 5 lb./100 ft² when dissolved in alkali metal formate brine at a
20 concentration of 2 pounds per barrel and measured at 120 degrees F.
Moreover, this advantageous viscosity is durable, in that the aqueous
polymeric compositions retain at least 50% of its apparent viscosity after roller
aging for 30 days at 375 degrees F and measured at 120 degrees F. As
discussed elsewhere herein, it should be understood that reference to a cesium
25 brine means a brine in which cesium carboxylate is the only or the primary
salt. Brines in which cesium carboxylate is the primary salt have only trace or
minor amounts of other salts, such as would be introduced through the use of

seawater in the polymer composition. Corresponding meanings apply for potassium brine, sodium brine, etc.

Preferably the water soluble copolymer is an AMPS copolymer prepared as the reaction product of 2-acrylamido-2-methylpropanesulfonic acid or salt thereof, most preferably 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid or salt thereof, with acrylamide, vinylpyrrolidone, acrylic acid or salt thereof. Optionally, a crosslinker reactant also is employed to achieve a higher molecular weight copolymer reaction product. Alternatively, reaction conditions may be controlled or other techniques employed to achieve a desired molecular weight without the use of a cross-linking agent. When used, the cross-linking agent should be at least bifunctional, such as N,N'-methylenebis[2-propenamide]. The water soluble copolymer preferably has about 5 to 95 wt.%, more preferably about 40 to 80 wt.% structural units derived from the 2-acrylamido-2-methylpropanesulfonic acid or salt thereof, or like reactant, and about 5 to 95 wt.%, more preferably about 20 to 60 wt.% structural units derived from the acrylic acid or its salt or like reactant, and about 0 to 5 wt.%, more preferably about 0 to 0.1 wt.% structural units derived from the cross-linking agent. Preferred salts of the copolymer include, for example, alkali metal salts, ammonium salts and the like.

An aqueous polymer composition suitable for use as a well service fluid, comprises the polymer composition described above together with water or brine solution in an amount preferably sufficient to substantially fully hydrate the water soluble copolymer and to dissolve the alkali metal salt of carboxylic acid.

In accordance with preferred embodiments, the water soluble copolymer is present in an amount of about 0.05 to 5.0 wt.%, based on the combined weight of all of the dry ingredients of the polymer composition period reference here to the dry ingredients means the undissolved salt(s), non-

hydrated copolymer, and any other solids of the polymer composition in the absence of water. Typically, therefore, the dry ingredients will include the copolymer, alkali metal salt of carboxylic acid, the solids content of any additives, etc. The alkali metal salt in such preferred embodiments is present
5 in an amount of about 95 to 99.95 wt.%, again based on the combined weight of the dry ingredients. These amounts are stated for the dry ingredients, not including the water content of any polymer compositions disclosed here which are aqueous polymer compositions.

The polymer compositions may further comprise other suitable
10 ingredients, including, for example, alkali metal salts of at least 1 halide. Thus, for example, the polymer compositions may incorporate the sodium, potassium and/or cesium salts of chloride, bromide or mixtures thereof. In addition, minor amounts of suitable additive may be present in the polymer compositions, including for example, any of the additives currently known for
15 use in well servicing fluids of this general type.

The water soluble copolymer can be prepared in accordance with known polymerization techniques. Preferably, 2-acrylamido-2-methylpropanesulfonic acid or like AMPS reactant is polymerized together with acrylic acid or other suitable carboxylic acid, after which the resulting
20 water soluble copolymer is optionally neutralized to the salt by addition of suitable ammonium, sodium or calcium compound or the like. It should be understood that the term water swellable and water soluble is used herein to include both the dry and the hydrated form of the copolymer, unless otherwise clearly indicated by context. As such, it will be recognized that the term
25 water-soluble refers to the hydrophilic nature of the copolymer whether or not the polymer is in the hydrated form. It should also be recognized that the term acrylic acid is used here interchangeably with propanoic acid.

The invention will be further understood from the following illustrative Examples.

Example I

5 To an 83% cesium formate (2.286 s.g.) solution buffered to pH 10.0 the copolymer disclosed above is added in the amount of 6 lb/bbl by the following procedure which substantially follows "*Recommended Practice Standard Procedure for Field Testing Water-Based Drilling Fluids*" API Recommended Practice 13B-1 (RP 13B-1) First Edition, June 1, 1990
10 (American National Standard, ANSI/API RP 13B-1-90 Approved: July 12, 1993). The procedure used commences with weighing the required amount of dry polymer and the required amount of cesium formate solution. Then, using an Air mixer equipped with a 1.25 inch high efficiency paddle assembly the copolymer powder is slowly added to the cesium formate solution while
15 mixing at medium speed. When all the powder is added the mixer speed is increased to approximately 4000 rpm. The sample is left mixing overnight. The sample is poured in a cup and the unaged viscosities are read using an OFITE Model 800 Viscometer. The sample is then poured into a stainless steel gas tight Aging Cell lined with Teflon cup. The Aging Cell is placed in a
20 roller oven pre-heated to 375°F. The sample is hot rolled for 24 hrs; after 24 hours the sample is cooled down to 120 °F and the viscosities are read. The Apparent Viscosity, Plastic Viscosity and Yield Point of the aged sample are then calculated. The sample is then poured back in the Aging Cell and continually aged at 375°F for the specified test period (i.e., 48, 96, 168, 336,
25 504, 672 and 744 hours).

After each test period, the sample is cooled and the measurements conducted at 120°F. The results are tabulated in Table 1, below, and charted in Fig. 1.

Table 1

Hot Rolled at 375°F(hours)	16	24	48	168	336	504	672	744
Apparent Viscosity (cP)	61	59	56.5	50	50	48	46	46
Plastic Viscosity (cP)	48	47	45	40	40	39	37	37
Yield Point (lbs/100sq.ft.)	26	24	23	20	20	18	18	18

Example 2

- 5 To a blend of potassium formate and cesium formate (1.88 s.g.) mixed in the ratio of 1:1.27 solution, buffered to pH 10.0, the copolymer disclosed above is added in the amount of 6 lb/bbl by following the same procedure as described in Example 1. The results of apparent viscosity, plastic viscosity and yield point are measured at the time intervals indicated in Table 2, below.
- 10 The results are charted in Fig. 2.

Table 2

Hot Rolled at 375°F(hours)	16	24	48	168	336	504	672	744
Apparent Viscosity (cP)	63	58	56	54.5	45.5	44.5	43.5	43
Plastic Viscosity (cP)	51	48	46	-	39	39	38	37
Yield Point (lbs/100sq.ft.)	-	31	24	18	17	17	15	16

Example 3

- Copolymer, as disclosed above, was prepared by mixing the
- 15 ingredients shown in Table 3 in the amounts indicated.

Table 3

	Deionized water	355.79
	Acrylic acid	235.37
20	AMPS	169.25
	Methylenebisacrylamide	.012
	Aqueous ammonia	239.35
	Sodium persulfate	.17
	Sodium bromate	.02
25	Sodium metabisulfite	.04

The "AMPS" ingredient listed in Table 3 was 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid. The deionized water was used to dissolve solid ingredients before mixing. The mixture underwent polymerization reaction in accordance with known techniques. The resultant water soluble copolymer was suitable for use in applications such as well servicing fluids.

Example 4

In a field operation in the North Sea, a viscous cesium formate slug (2.18 s.g.) was prepared for pumping into a well as part of a completion operation. The viscous cesium formate slug was formed with 6 lbs. per barrel of the water soluble copolymer formed in accordance with Example 3. The well had a bottom hole temperature of 400°F. The viscous cesium formate slug was pumped to the bottom of the drill hole. The polymer composition was used as a viscous pill to sweep the well of particulate matter and downhole debris. In this function it worked well, displacing debris to the surface and leaving a clean well bore for the next stage of the completion operation. The viscous cesium formate was found to have substantially no loss of viscosity when returned to the surface and recovered after several hours of use.

In light of the foregoing disclosure of the invention and description of the preferred embodiments, those skilled in this area of technology will readily understand that various modifications and adaptations can be made without departing from the true scope and spirit of the invention. All such modifications and adaptations are intended to be covered by the following claims.

We Claim:

1. A polymer composition comprising:
water soluble copolymer having functionality including at least
5 sulfonate groups and carboxylate groups; and
alkali metal salt of carboxylic acid.
2. The polymer composition of claim 1 wherein the water soluble
10 copolymer has a weight average molecular weight of at least 1,000,000.
3. The polymer composition of claim 1 wherein the water soluble
copolymer has weight average molecular weight between 1,000,000 and
5,000,000.
- 15 4. The polymer composition of claim 1 wherein the water soluble
copolymer is soluble in an amount of at least 4 lbs/bbl in a substantially
saturated brine of alkali metal carboxylate selected from sodium, potassium
and cesium salts of acetic and formic acids.
- 20 5. A polymer composition comprising:
water soluble copolymer formed as the polymerization reaction product
of acrylamidomethylpropanesulfonic acid or salt thereof and alpha, beta-
unsaturated carbonyl compound; and
alkali metal salt of carboxylic acid.
- 25 6. The polymer composition of claim 5 wherein the alkali metal salt of
carboxylic acid is selected from the sodium, potassium and cesium salts of C1
to C3 carboxylic acid.
- 30 7. The polymer composition of claim 5 wherein the alkali metal salt of
carboxylic acid is selected from alkali metal salts of formic acid, acetic acid
and mixtures thereof.

14

8. The polymer composition of claim 5 wherein the acrylamidomethylpropanesulfonic acid or salt thereof is 2-acrylamido-2-methylpropanesulfonic acid or salt thereof.

5 9. The polymer composition of claim 5 wherein the acrylamidomethylpropanesulfonic acid or salt thereof is 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid or salt thereof.

10 10. The polymer composition of claim 5 wherein the water soluble copolymer comprises from 5 to 95 wt.% structural units derived from 2-acrylamido-2-methylpropanesulfonic acid or salt thereof, and from 5 to 95 wt.% structural units derived from acrylamide, vinylpyrrolidone, acrylic acid or salt thereof; and
the alkali metal salt comprises at least one alkali metal salt of C1 to C3
15 carboxylic acid.

11. A polymer composition of claim 10 wherein the water soluble copolymer has 5 to 95 wt.% structural units derived from 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid or salt thereof, and 5 to 95 wt.%
20 structural units derived from 2-propanoic acid or salt thereof.

12. The polymer composition of claim 10 wherein the alkali metal salt is primarily cesium salt.

25 13. The polymer composition of claim 11 having 0 to 5 wt.% structural units derived from an at least bifunctional cross-linking agent.

14. The polymer composition of claim 13 wherein the cross-linking agent is N,N'-methylenebis[2-propenamide].

30

15. The polymer composition of claim 10 wherein the water soluble copolymer is present in an amount of 0.05 to 5 wt.% of the combined weight

15

of all solids of the polymer composition and the alkali metal salt is present in an amount of 95 to 99.95 wt.% of the combined weight of all solids of the polymer composition.

5 16. The polymer composition of claim 5 wherein the copolymer is substantially hydrated by water and the alkali metal salt of carboxylic acid is substantially dissolved.

10 17. The polymer composition of claim 16 further comprising alkali metal salt of at least 1 halide.

15 18. The polymer composition of claim 16 wherein the alkali metal salt of at least 1 halide is selected from the sodium, potassium and cesium salts of chloride, bromide and mixtures thereof.

20 19. The polymer composition of claim 16 developing an apparent viscosity of at least 20 cPs., a plastic viscosity of at least 15 cPs, and a yield point of at least 5 lb./100 ft² when dissolved in cesium formate brine at a concentration of 2 pounds per barrel and measured at 120 degrees F.

25 20. The polymer composition of claim 19 retaining at least 50 percent of its apparent viscosity after roller aging for 30 days at 375 degrees F and measured at 120 degrees F.

30 21. A process for preparing an aqueous polymer composition according to claim 16 comprising hydrating the polymer composition.

22. A process for preparing an aqueous polymer composition according to claim 21 wherein alkali metal salt of carboxylic acid is dissolved aqueous composition containing the water soluble copolymer.

23. A process for preparing an aqueous polymer composition according to claim 21 wherein the water soluble copolymer is dissolved in a brine of alkali metal salt of carboxylic acid.
- 5 24. A method of carrying out well-drilling or well-servicing operations comprising the use of an aqueous well service fluid comprising water soluble copolymer having functionality including at least sulfonate groups and carboxylate groups, hydrated in a brine solution.
- 10 25. The method of claim 24 wherein the water soluble copolymer is substantially fully hydrated in the brine solution.
26. An aqueous well service fluid comprising:
water soluble copolymer having functionality including at least
15 sulfonate groups and carboxylate groups, hydrated in a brine solution.
27. The aqueous well servicing fluid of claim 26 wherein the water soluble copolymer is soluble in a brine of alkali metal salt of carboxylic acid.
- 20 28. The aqueous well servicing fluid of claim 26 wherein the water soluble copolymer is substantially fully hydrated in the brine solution.
29. Water soluble copolymer having functionality including at least sulfonate groups and carboxylate groups, which has a weight average
25 molecular weight of at least 1,000,000 and develops an apparent viscosity of at least 20 cPs., a plastic viscosity of at least 15 cPs, and a yield point of at least 5 lb./100 ft² when substantially fully hydrated in cesium formate brine at a concentration of 2 pounds per barrel and measured at 120 degrees F.
- 30 30. Water soluble copolymer of claim 29 having weight average molecular weight between 1,000,000 and 5,000,000.

31. Water soluble copolymer of claim 29 soluble in an amount of at least 4 lbs/bbl in a substantially saturated brine of alkali metal carboxylate selected from sodium, potassium and cesium salts of acetic and formic acids.
32. Water soluble copolymer of claim 29 which retains at least 50 percent of its apparent viscosity after roller aging for 30 days at 375 degrees F and measured at 120 degrees F.
33. Water soluble copolymer of claim 29 hydrated in a brine solution.
34. Water soluble copolymer comprising the polymerization reaction product of acrylamidomethylpropanesulfonic acid or salt thereof and alpha,beta-unsaturated carbonyl compound, having weight average molecular weight of at least 1,000,000 and developing an apparent viscosity of at least 20 cPs, a plastic viscosity of at least 15 cPs, and a yield point of at least 5 lb./100 ft² when substantially fully hydrated in cesium formate brine at a concentration of 2 pounds per barrel and measured at 120 degrees F.
35. Water soluble copolymer of claim 34 wherein the acrylamidomethylpropanesulfonic acid or salt thereof is 2-acrylamido-2-methylpropanesulfonic acid or salt thereof.
36. Water soluble copolymer of claim 34 wherein the acrylamidomethylpropanesulfonic acid or salt thereof is 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid or salt thereof.
37. Water soluble copolymer of claim 34 having 5 to 95 wt.% structural units derived from 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid or salt thereof, and 5 to 95 wt.% structural units derived from 2-propanoic acid or salt thereof.

18

38. Water soluble copolymer of claim 34 having 40 to 80 wt.% structural units derived from 2-acrylamido-2-methylpropanesulfonic acid or salt thereof and 20 to 60 wt.% structural units derived from acrylamide, vinylpyrrolidone, acrylic acid or salt thereof.

5

39. Water soluble copolymer of claim 38 having 0 to 5 wt.% structural units derived from an at least bifunctional cross-linking agent.

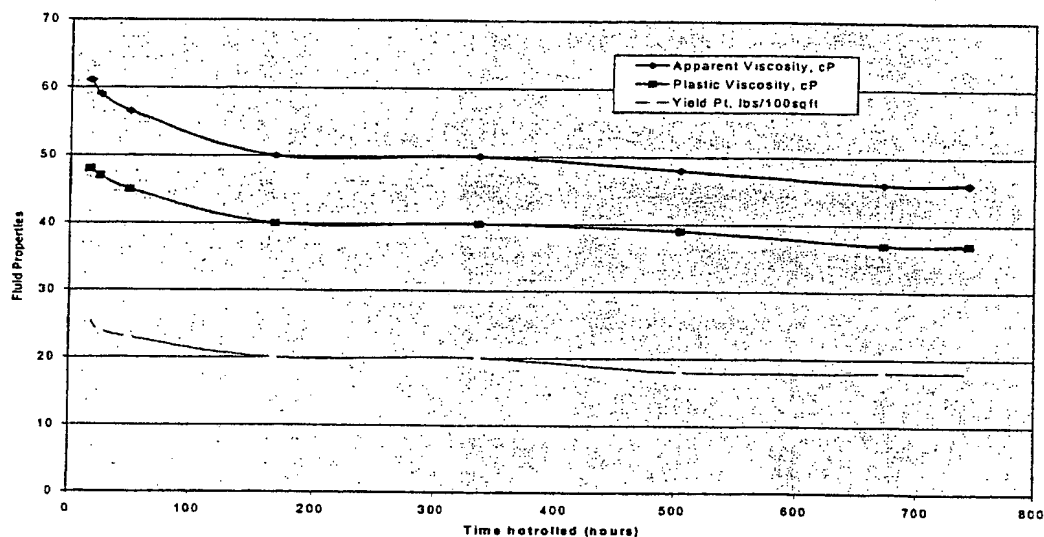


Figure 1

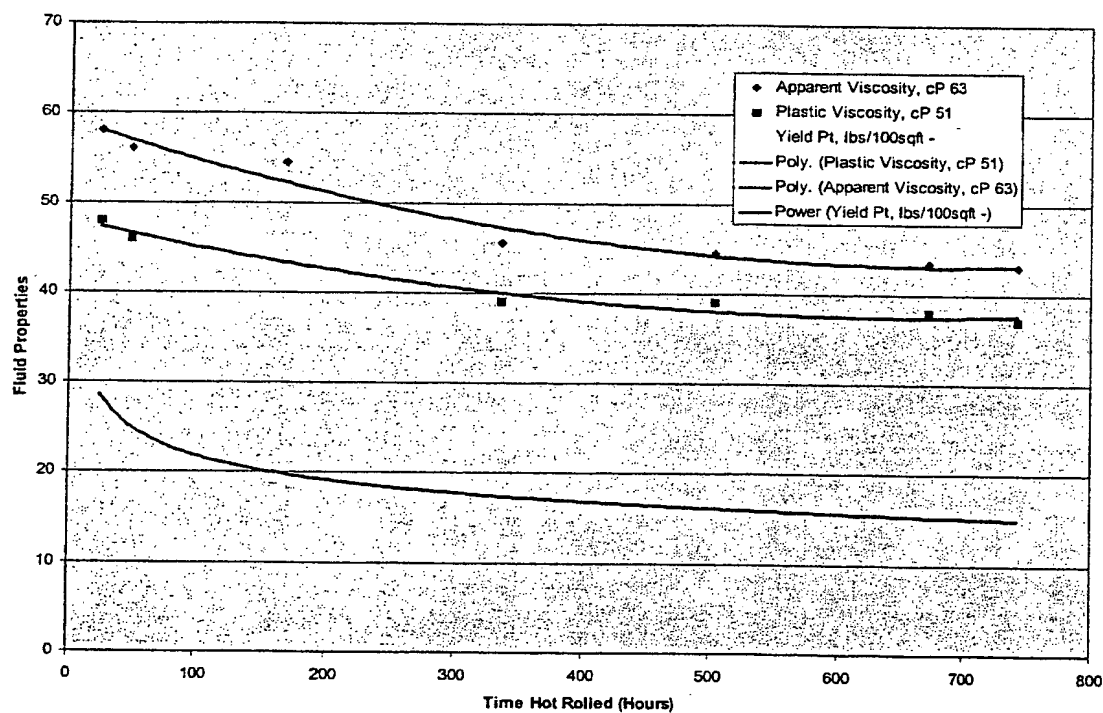


Figure 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/13727

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09K7/02 C08K5/098 C08L33/24		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09K C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 04348 A (BAKER HUGHES INC.) 15 February 1996 (1996-02-15) table 7A page 16, line 15,16 claim 7 page 10, line 14 -page 11, line 9 page 12, line 9 - line 19 page 17, line 17 - line 22 ---	1-8,10, 21-28
X	EP 0 621 329 A (SHELL INT RESEARCH) 26 October 1994 (1994-10-26) column 3, line 9 - line 22 --- -/--	1-8,10, 16-19, 21-29, 34,35,38
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 31 July 2000		Date of mailing of the international search report 08/08/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Friederich, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/13727

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	DE 198 40 632 A (CLARIANT GMBH) 9 March 2000 (2000-03-09) examples; table 1 ----	1-8, 10, 16-19, 22, 23, 25-29, 34, 35, 38
A	US 5 620 947 A (ELWARD-BERRY JULIANNE) 15 April 1997 (1997-04-15) examples column 7, line 6-30 ----	1-39
A	EP 0 572 113 A (BP CHEM INT LTD) 1 December 1993 (1993-12-01) examples; tables ----	24-39
A	WO 99 23188 A (GREAT LAKES CHEMICAL CORP ; HORTON ROBERT L (US); VOLLMER DANIEL P) 14 May 1999 (1999-05-14) example 10 page 15, line 9 - line 12 -----	1-39

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal. Application No

PCT/US 00/13727

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9604348 A	15-02-1996	AU 3149495 A	04-03-1996
EP 0621329 A	26-10-1994	AU 675712 B	13-02-1997
		AU 6720894 A	08-11-1994
		CA 2161024 A	27-10-1994
		DE 69404978 D	18-09-1997
		DE 69404978 T	18-12-1997
		DK 695333 T	30-03-1998
		WO 9424224 A	27-10-1994
		EP 0695333 A	07-02-1996
		NO 954182 A	19-10-1995
		NZ 266135 A	25-09-1996
DE 19840632 A	09-03-2000	EP 0992563 A	12-04-2000
		NO 994291 A	07-03-2000
US 5620947 A	15-04-1997	NONE	
EP 0572113 A	01-12-1993	DE 69300541 D	02-11-1995
		DE 69300541 T	21-03-1996
		NO 931495 A	30-11-1993
WO 9923188 A	14-05-1999	AU 1382499 A	24-05-1999